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(54) Title: THERMALLY STABLE NONAZIDE AUTOMOTIVE AIRBAG PROPELLANTS			
(57) Abstract Thermally stable gas generant compositions incorporate a combination of nitroguanidine, one or more nonazide high-nitrogen fuels, and phase-stabilized ammonium nitrate or a similar nonmetallic oxidizer that, upon combustion, result in a greater yield of gaseous products per mass unit of gas generant, a reduced yield of solid combustion products, and acceptable burn rates, thermal stability, and ballistic properties. These compositions are especially suitable for inflating air bags in passenger-restraint devices.			

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THERMALLY STABLE NONAZIDE AUTOMOTIVE AIRBAG PROPELLANTSCROSS-REFERENCE TO RELATED APPLICATIONS

The present application is a continuation-in-part of
5 U.S. Patent Application Serial No. 08/681,662, filed on July
29, 1996.

BACKGROUND OF THE INVENTIONField of the Invention

The present invention relates to nontoxic gas
generating compositions which upon combustion, rapidly generate
5 gases that are useful for inflating occupant safety restraints
in motor vehicles and specifically, the invention relates to
thermally stable nonazide gas generants having not only
acceptable burn rates, but that also, upon combustion, exhibit
a relatively high gas volume to solid particulate ratio at
10 acceptable flame temperatures.

The evolution from azide-based gas generants to
nonazide gas generants is well-documented in the prior art.
The advantages of nonazide gas generant compositions in
comparison with azide gas generants have been extensively
15 described in the patent literature, for example, U.S. Patents
No. 4,370,181; 4,909,549; 4,948,439; 5,084,118; 5,139,588 and
5,035,757, the discussions of which are hereby incorporated by
reference.

In addition to a fuel constituent, pyrotechnic
20 nonazide gas generants contain ingredients such as oxidizers to
provide the required oxygen for rapid combustion and reduce the
quantity of toxic gases generated, a catalyst to promote the
conversion of toxic oxides of carbon and nitrogen to innocuous
gases, and a slag forming constituent to cause the solid and
25 liquid products formed during and immediately after combustion
to agglomerate into filterable clinker-like particulates.
Other optional additives, such as burning rate enhancers or
ballistic modifiers and ignition aids, are used to control the
ignitability and combustion properties of the gas generant.

30 One of the disadvantages of known nonazide gas

generant compositions is the amount and physical nature of the solid residues formed during combustion. The solids produced as a result of combustion must be filtered and otherwise kept away from contact with the occupants of the vehicle. It is
5 therefore highly desirable to develop compositions that produce a minimum of solid particulates while still providing adequate quantities of a nontoxic gas to inflate the safety device at a high rate.

The use of phase stabilized ammonium nitrate is
10 desirable because it generates abundant nontoxic gases and minimal solids upon combustion. To be useful, however, gas generants for automotive applications must be thermally stable when aged for 400 hours or more at 107°C. The compositions must also retain structural integrity when cycled between -40°C
15 and 107°C.

Often, gas generant compositions incorporating phase stabilized or pure ammonium nitrate exhibit poor thermal stability, and produce unacceptably high levels of toxic gases, CO and NO_x for example, depending on the composition of the
20 associated additives such as plasticizers and binders. In addition, ammonium nitrate contributes to poor ignitability, lower burn rates, and performance variability. Several known gas generant compositions incorporating ammonium nitrate utilize well known ignition aids such as BKNO₃ to solve this
25 problem. However, the addition of an ignition aid such as BKNO₃ is undesirable because it is a highly sensitive and energetic compound, and furthermore, contributes to thermal instability and an increase in the amount of solids produced.

Certain gas generant compositions comprised of
30 ammonium nitrate are thermally stable, but have burn rates less than desirable for use in gas inflators. To be useful for passenger restraint inflator applications, gas generant compositions generally require a burn rate of at least .4 inch/second (ips) or more at 1000 psi. Gas generants with burn
35 rates of less than 0.40 ips at 1000 psi do not ignite reliably and often result in "no-fires" in the inflator.

Yet another problem that must be addressed is that

the U.S. Department of Transportation (DOT) regulations require "cap testing" for gas generants. Because of the sensitivity to detonation of fuels often used in conjunction with ammonium nitrate, most propellants incorporating ammonium nitrate do not
5 pass the cap test unless shaped into large disks, which in turn reduces design flexibility of the inflator.

Accordingly, many nonazide propellants based on ammonium nitrate cannot meet requirements for automotive applications.

10 Description of the Related Art

A description of the related art follows, the complete teachings of which are herein incorporated by reference.

U.S. Patent No. 5,545,272 to Poole discloses the use
15 of gas generant compositions consisting of nitroguanidine (NQ), at a weight percent of 35%-55%, and phase stabilized ammonium nitrate (PSAN) at a weight percent of 45%-65%. NQ, as a fuel, is preferred because it generates abundant gases and yet consists of very little carbon or oxygen, both of which
20 contribute to higher levels of CO and NOx in the combustion gases. According to Poole, the use of phase stabilized ammonium nitrate (PSAN) or pure ammonium nitrate is problematic because many gas generant compositions containing the oxidizer are thermally unstable. Poole has found that combining NQ and
25 PSAN in the percentages given results in thermally stable gas generant compositions. However, Poole reports burn rates of only .32 -.34 inch per second, at 1000 psi. As is well known, burn rates below .4 inch per second at 1000 psi are simply too low for confident use within an inflator.

30 In U.S. Patent No. 5,531,941 to Poole, Poole teaches the use of PSAN, and two or more fuels selected from a specified group of nonazide fuels. Poole adds that gas generants using ammonium nitrate (AN) as the oxidizer are generally very slow burning with burning rates at 1000 psi
35 typically less than 0.1 inch per second. He further teaches that for air bag applications, burning rates of less than about 0.4 to 0.5 inch per second are difficult to use. The use of

PSAN is taught as desirable because of its propensity to produce abundant gases and minimal solids, with minimal noxious gases. Nevertheless, Poole recognizes the problem of low burn rates and thus combines PSAN with a fuel component containing a majority of TAGN, and if desired one or more additional fuels. The addition of TAGN increases the burn rate of ammonium nitrate mixtures. According to Poole, TAGN/PSAN compositions exhibit acceptable burn rates of .59-.83 inch/per second. TAGN, however, is a sensitive explosive that poses safety concerns in processing and handling. In addition, TAGN is classified as "forbidden" by the Department of Transportation, therefore complicating raw material requirements.

In U.S. Patent No. 5,500,059 to Lund et al., Lund states that burn rates in excess of 0.5 inch per second (ips) at 1,000 psi, and preferably in the range of from about 1.0 ips to about 1.2 ips at 1,000 psi, are generally desired. Lund discloses gas generant compositions comprised of a 5-aminotetrazole fuel and a metallic oxidizer component. The use of a metallic oxidizer reduces the amount of gas liberated per gram of gas generant, however, and increases the amount of solids generated upon combustion.

The gas generant compositions described in Poole et al, U.S. Patents No. 4,909,549 and 4,948,439, use tetrazole or triazole compounds in combination with metal oxides and oxidizer compounds (alkali metal, alkaline earth metal, and pure ammonium nitrates or perchlorates) resulting in a relatively unstable generant that decomposes at low temperatures. Significant toxic emissions and particulate are formed upon combustion. Both patents teach the use of BKNO₃ as an ignition aid.

The gas generant compositions described in Poole, U.S. Patent No. 5,035,757, result in more easily filterable solid products but the gas yield is unsatisfactory.

Chang et al, U.S. Patent No. 3,954,528, describes the use of TAGN and a synthetic polymeric binder in combination with an oxidizing material. The oxidizing materials include

pure AN although, the use of PSAN is not suggested. The patent teaches the preparation of propellants for use in guns or other devices where large amounts of carbon monoxide, nitrogen oxides, and hydrogen are acceptable and desirable. Because of
5 the practical applications involved, thermal stability is not considered a critical parameter.

Grubaugh, U.S. Patent No. 3,044,123, describes a method of preparing solid propellant pellets containing AN as the major component. The method requires use of an oxidizable
10 organic binder (such as cellulose acetate, PVC, PVA, acrylonitrile and styrene-acrylonitrile), followed by compression molding the mixture to produce pellets and by heat treating the pellets. These pellets would certainly be damaged by temperature cycling because commercial ammonium nitrate is
15 used, and the composition claimed would produce large amounts of carbon monoxide.

Becuwe, U.S. Patent No. 5,034,072, is based on the use of 5-oxo-3-nitro-1,2,4-triazole as a replacement for other explosive materials (HMX, RDX, TATB, etc.) in propellants and
20 gun powders. This compound is also called 3-nitro-1,2,4-triazole-5-one ("NTO"). The claims appear to cover a gun powder composition which includes NTO, AN and an inert binder, where the composition is less hygroscopic than a propellant containing ammonium nitrate. Although called inert, the binder
25 would enter into the combustion reaction and produce carbon monoxide making it unsuitable for air bag inflation.

Lund et al, U.S. Patent No. 5,197,758, describes gas generating compositions comprising a nonazide fuel which is a transition metal complex of an aminoarazole, and in particular
30 are copper and zinc complexes of 5-aminotetrazole and 3-amino-1,2,4-triazole which are useful for inflating air bags in automotive restraint systems, but generate excess solids.

Wardle et al, U.S. Patent No. 4,931,112, describes an automotive air bag gas generant formulation consisting
35 essentially of NTO (5-nitro-1,2,4-triazole-3-one) and an oxidizer wherein said formulation is anhydrous.

Ramnarace, U.S. Patent No. 4,111,728, describes gas

generators for inflating life rafts and similar devices or that are useful as rocket propellants comprising ammonium nitrate, a polyester type binder and a fuel selected from oxamide and guanidine nitrate. Ramnarace teaches that ammonium nitrate
5 contributes to burn rates lower than those of other oxidizers and further adds that ammonium nitrate compositions are hygroscopic and difficult to ignite, particularly if small amounts of moisture have been absorbed.

Bucerius et al, U.S. Patent No. 5,198,046, teaches
10 the use of diguanidinium-5,5'-azotetrazolate (GZT) with KNO_3 as an oxidizer, for use in generating environmentally friendly, non-toxic gases. Bucerius teaches away from combining GZT with any chemically unstable and/or hygroscopic oxidizer. The use of other amine salts of tetrazole such as bis-
15 (triaminoguanidinium)-5,5'-azotetrazolate (TAGZT) or aminoguanidinium-5,5'-azotetrazolate are taught as being much less thermally stable when compared to GZT.

Boyars, U.S. Patent No. 4,124,368, describes a method
20 for preventing detonation of ammonium nitrate by using potassium nitrate.

Mishra, U.S. Patent No. 4,552,736, and Mehrotra et al, U.S. Patent No. 5,098,683, describe the use of potassium fluoride to eliminate expansion and contraction of ammonium nitrate in transition phase.

25 Chi, U.S. Patent No. 5,074,938, describes the use of phase stabilized ammonium nitrate as an oxidizer in propellants containing boron and as useful in rocket motors.

In U.S. Patent 5,125,684 to Cartwright, an extrudable propellant for use in crash bags is described as comprising an
30 oxidizer salt, a cellulose-based binder and a gas generating component. Cartwright also teaches the use of "at least one energetic component selected from nitroguanidine (NG), triaminoguanidine nitrate, ethylene dinitramine, cyclotrimethylenetrinitramine (RDX),
35 cyclotetramethylenetetranitramine (HMX), trinitrotoluene (TNT), and pentaerythritol tetranitrate (PETN)...."

In U.S. Patent 4,925,503 to Canterbury et al, an

explosive composition is described as comprising a high energy material, e.g., ammonium nitrate and a polyurethane polyacetal elastomer binder, the latter component being the focus of the invention. Canterbury also teaches the use of a "high energy
5 material useful in the present invention ... preferably one of the following high energy materials: RDX, NTO, TNT, HMX, TAGN, nitroguanidine, or ammonium nitrate..."

Hass, U.S. Patent No. 3,071,617, describes long known considerations as to oxygen balance and exhaust gases.

10 Stinecipher et al, U.S. Patent No. 4,300,962, describes explosives comprising ammonium nitrate and an ammonium salt of a nitroazole.

Prior, U.S. Patent No. 3,719,604, describes gas generating compositions comprising aminoguanidine salts of
15 azotetrazole or of ditetrazole.

Poole, U.S. Patent No. 5,139,588, describes nonazide gas generants useful in automotive restraint devices comprising a fuel, an oxidizer and additives.

Hendrickson, U.S. Patent No. 4,798,637, teaches the
20 use of bitetrazole compounds, such as diammonium salts of bitetrazole, to lower the burn rate of gas generant compositions. Hendrickson describes burn rates below .40 ips, and an 8% decrease in the burn rate when diammonium bitetrazole is used.

25 Chang et al, U.S. Patent No. 3,909,322, teaches the use of nitroaminotetrazole salts with oxidizers such as pure ammonium nitrate, HMX, and 5-ATN. These compositions are used as gun propellants and gas generants for use in gas pressure actuated mechanical devices such as engines, electric
30 generators, motors, turbines, pneumatic tools, and rockets. In contrast to the amine salts disclosed by Hendrickson, Chang teaches that gas generants comprised of 5-aminotetrazole nitrate and salts of nitroaminotetrazole exhibit burn rates in excess of .40 ips. On the other hand, Chang also teaches that
35 gas generants comprised of HMX and salts of nitroaminotetrazole exhibit burn rates of .243 ips to .360 ips. No data is given with regard to burn rates associated with pure AN and salts of

nitroaminotetrazole.

Highsmith et al, U.S. Patent No. 5,516,377, teaches the use of a salt of 5-nitraminotetrazole, NQ, a conventional ignition aid such as BKNO₃, and pure ammonium nitrate as an oxidizer, but does not teach the use of phase stabilized ammonium nitrate. Highsmith states that a composition comprised of ammonium nitraminotetrazole and strontium nitrate exhibits a burn rate of .313 ips. This is too low for automotive application. As such, Highsmith emphasizes the use of metallic salts of nitraminotetrazole.

Onishi et al, U.S. Patent No. 5,439,251, teaches the use of a tetrazole amine salt as an air bag gas generating agent comprising a cationic amine and an anionic tetrazolyl group having either an alkyl with carbon number 1-3, chlorine, hydroxyl, carboxyl, methoxy, aceto, nitro, or another tetrazolyl group substituted via diazo or triazo groups at the 5-position of the tetrazole ring. The inventive thrust is to improve the physical properties of tetrazoles with regard to impact and friction sensitivity, and therefore does not teach the combination of an amine or nonmetal tetrazole salt with any other chemical.

Lund et al, U.S. Patent No. 5,501,823, teaches the use of nonazide anhydrous tetrazoles, derivatives, salts, complexes, and mixtures thereof, for use in air bag inflators. The use of bitetrazole-amines, not amine salts of bitetrazoles, is also taught.

Based on the above, the need remains for a PSAN-based gas generant which is thermally stable at 107C, ignites readily and without delay, has a burn rate at 1000psi of greater than 0.40-0.50ips, and contains no sensitive explosive compounds.

SUMMARY OF THE INVENTION

The aforementioned problems are solved by a nonazide gas generant for a vehicle passenger restraint system comprising phase stabilized ammonium nitrate, nitroguanidine, and one or more nonazide fuels. The nonazide fuels are selected from a group including guanidines; tetrazoles such as

5,5'-bitetrazole, diammonium bitetrazole, diguanidinium-5,5'-azotetrazolate (GZT), and nitrotetrazoles such as 5-nitrotetrazole; triazoles such as nitroaminotriazole, nitrotriazoles, and 3-nitro-1,2,4 triazole-5-one; and salts of tetrazoles and triazoles.

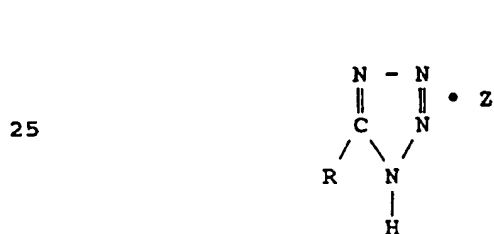
A preferred fuel(s) is selected from the group consisting of amine and other nonmetal salts of tetrazoles and triazoles having a nitrogen containing cationic component and a tetrazole and/or triazole anionic component. The anionic component comprises a tetrazole or triazole ring, and an R group substituted on the 5-position of the tetrazole ring, or two R groups substituted on the 3- and 5-positions of the triazole ring. The R group(s) is selected from hydrogen and any nitrogen-containing compounds such as amino, nitro, nitramino, tetrazolyl and triazolyl groups. The cationic component is formed from a member of a group including amines, aminos, and amides including ammonia, hydrazine, guanidine compounds such as guanidine, aminoguanidine, diaminoguanidine, triaminoguanidine, dicyandiamide, nitroguanidine, nitrogen substituted carbonyl compounds such as urea, carbohydrazide, oxamide, oxamic hydrazide, bis-(carbonamide) amine, azodicarbonamide, and hydrazodicarbonamide, and, amino azoles such as 3-amino-1,2,4-triazole, 3-amino-5-nitro-1,2,4-triazole, 5-aminotetrazole and 5-nitraminotetrazole. Optional inert additives such as clay, alumina, or silica may be used as a binder, slag former, coolant or processing aid. Optional ignition aids comprised of nonazide propellants may also be utilized in place of conventional ignition aids such as BKNO.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENT(S)

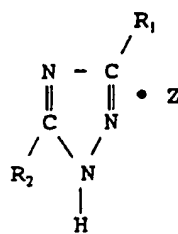
A nonazide gas generant comprises phase stabilized ammonium nitrate (PSAN), nitroguanidine (NQ), and one or more nonazide high-nitrogen fuels. One or more high-nitrogen fuels are selected from a group including tetrazoles such as 5-nitrotetrazole, 5,5'-bitetrazole, triazoles such as nitroaminotriazole, nitrotriazoles, nitrotetrazoles, salts of tetrazoles and triazoles, and 3-nitro-1,2,4 triazole-5-one.

More specifically, salts of tetrazoles include in particular, amine, amino, and amide salts of tetrazole and triazole selected from the group including monoguanidinium salt of 5,5'-Bis-1H-tetrazole (BHT·1GAD), diguanidinium salt of 5,5'-Bis-1H-tetrazole (BHT·2GAD), monoaminoguanidinium salt of 5,5'-Bis-1H-tetrazole (BHT·1AGAD), diaminoguanidinium salt of 5,5'-Bis-1H-tetrazole (BHT·2AGAD), monohydrazinium salt of 5,5'-Bis-1H-tetrazole (BHT·1HH), dihydrazinium salt of 5,5'-Bis-1H-tetrazole (BHT·2HH), monoammonium salt of 5,5'-bis-1H-tetrazole (BHT·1NH₃), diammonium salt of 5,5'-bis-1H-tetrazole (BHT·2NH₃), mono-3-amino-1,2,4-triazolium salt of 5,5'-bis-1H-tetrazole (BHT·1ATAZ), di-3-amino-1,2,4-triazolium salt of 5,5'-bis-1H-tetrazole (BHT·2ATAZ), and diguanidinium salt of 5,5'-Azobis-1H-tetrazole (ABHT·2GAD).

Amine salts of triazoles include monoammonium salt of 3-nitro-1,2,4-triazole (NTA·1NH₃), monoguanidinium salt of 3-nitro-1,2,4-triazole (NTA·1GAD), diammonium salt of dinitrobitriazole (DNBTR·2NH₃), diguanidinium salt of dinitrobitriazole (DNBTR·2GAD), and monoammonium salt of 3,5-dinitro-1,2,4-triazole (DNTR·1NH₃).



Formula I



Formula II

A generic nonmetal salt of tetrazole as shown in Formula I includes a cationic nitrogen containing component, Z, and an anionic component comprising a tetrazole ring and an R group substituted on the 5-position of the tetrazole ring. A generic nonmetal salt of triazole as shown in Formula II includes a cationic nitrogen containing component, Z, and an anionic component comprising a triazole ring and two R groups substituted on the 3- and 5- positions of the triazole ring, wherein R₁ may or may not be structurally synonymous with R₂. An R component is selected from a group including hydrogen or

any nitrogen-containing compound such as an amino, nitro, nitramino, or a tetrazolyl or triazolyl group as shown in Formula I or II, respectively, substituted directly or via amine, diazo, or triazo groups. The compound Z is substituted
5 at the 1-position of either formula, and is formed from a member of the group comprising amines, aminos, and amides including ammonia, carbohydrazide, oxamic hydrazide, and hydrazine; guanidine compounds such as guanidine, aminoguanidine, diaminoguanidine, triaminoguanidine,
10 dicyandiamide and nitroguanidine; nitrogen substituted carbonyl compounds or amides such as urea, oxamide, bis-(carbonamide) amine, azodicarbonamide, and hydrazodicarbonamide; and, amino azoles such as 3-amino-1,2,4-triazole, 3-amino-5-nitro-1,2,4-triazole, 5-aminotetrazole, 3-nitramino-1,2,4-triazole, 5-
15 nitraminotetrazole, and melamine.

In accordance with the present invention, a preferred gas generant composition results from the mixture of gas generant constituents including nitroguanidine, comprising 1%-30% by weight of the gas generant composition, one or more
20 amine salts of tetrazoles and/or triazoles, comprising 4%-40% by weight of the gas generant composition, and PSAN, comprising 40%-85% by weight of the gas generant composition. In the percentages given, an even more preferred embodiment results from the mixture of gas generant constituents consisting
25 essentially of NQ, PSAN, and amine salt(s) of 5,5'-bis-1H-tetrazole. In the percentages given, a most preferred composition results from the mixture of gas generant constituents consisting essentially of NQ, PSAN, and diammonium salt of 5,5'-bis-1H-tetrazole ($\text{BHT} \cdot 2\text{NH}_3$). When combined, the
30 fuel component consisting of NQ and one or more high nitrogen fuels as described herein, comprises 15%-60% by weight of the gas generant composition.

In accordance with procedures well known in the art, the foregoing nonazide fuels, and/or nonmetal salts of
35 tetrazole or triazole, are blended with an oxidizer such as PSAN, and NQ. The manner and order in which the components of the gas generant compositions of the present invention are

combined and compounded is not critical so long as the proper particle size of ingredients are selected to ensure the desired mixture is obtained. The compounding is performed by one skilled in the art, under proper safety procedures for the preparation of energetic materials, and under conditions which will not cause undue hazards in processing nor decomposition of the components employed. For example, the materials may be wet blended, or dry blended and attrited in a ball mill or Red Devil type paint shaker and then pelletized by compression molding. The materials may also be ground separately or together in a fluid energy mill, sweco vibroenergy mill or bantam micropulverizer and then blended or further blended in a v-blender prior to compaction.

Compositions having components more sensitive to friction, impact, and electrostatic discharge should be wet ground separately followed by drying. The resulting fine powder of each of the components may then be wet blended by tumbling with ceramic cylinders in a ball mill jar, for example, and then dried. Less sensitive components may be dry ground and dry blended at the same time.

Phase stabilized ammonium nitrate is prepared as taught in co-owned U.S. Patent No. 5,531,941 entitled, "Process For Preparing Azide-free Gas Generant Composition". Other nonmetal inorganic oxidizers such as ammonium perchlorate, or oxidizers that produce minimal solids when combined and combusted with the fuels listed above, may also be used. The ratio of oxidizer to fuel is preferably adjusted so that the amount of oxygen allowed in the equilibrium exhaust gases is less than 3% by weight, and more preferably less than or equal to 2% by weight. The oxidizer comprises 40%-85% by weight of the gas generant composition.

The gas generant constituents of the present invention are commercially available. For example, the amine salts of tetrazoles may be purchased from Toyo Kasei Kogyo Company Limited, Japan. Nitroguanidine may be purchased from Nigu Chemie, and, the components used to synthesize PSAN, as described herein, may be purchased from Fisher or Aldrich.

Triazole salts may be synthesized by techniques, such as those described in U.S. Patent No. 4,236,014 to Lee et al.; in "New Explosives: Nitrotriazoles Synthesis and Explosive Properties", by H.H. Licht, H. Ritter, and B. Wanders, Postfach 1260, D-79574 Weil am Rhein; and in "Synthesis of Nitro Derivatives of Triazoles", by Ou Yuxiang, Chen Boren, Li Jiarong, Dong Shuan, Li Jianjun, and Jia Huiping, Heterocycles, Vol. 38, No. 7, pps. 1651-1664, 1994. The teachings of these references are herein incorporated by reference. Other compounds in accordance with the present invention may be obtained as taught in the references incorporated herein, or from other sources well known to those skilled in the art.

An optional burn rate modifier, from 0-10% by weight in the gas generant composition, is selected from a group including an alkali metal, an alkaline earth or a transition metal salt of tetrazoles or triazoles; an alkali metal or alkaline earth nitrate or nitrite; TAGN; dicyandiamide, and alkali and alkaline earth metal salts of dicyandiamide; alkali and alkaline earth borohydrides; or mixtures thereof. An optional combination slag former and coolant, in a range of 0 to 10% by weight, is selected from a group including clay, silica, glass, and alumina, or mixtures thereof. When combining the optional additives described, or others known to those skilled in the art, care should be taken to tailor the additions with respect to acceptable thermal stability, burn rates, and ballistic properties.

In accordance with the present invention, the combination of NQ, PSAN, and one or more nonazide high-nitrogen fuels, as determined by gravimetric procedures, yields beneficial gaseous products equal to or greater than 90% of the total product mass, and solid products equal to or lesser than 10% of the total product mass. Fuels suitable in practicing the present invention are high in nitrogen content and low in carbon content thereby providing a high burn rate and a minimal generation of carbon monoxide.

The synergistic effect of the high-nitrogen fuels, in combination with an oxidizer producing minimal solids when

combined with the fuels, results in several long-awaited benefits. Increased gas production per mass unit of gas generant results in the use of a smaller chemical charge. Reduced solids production results in minimized filtration needs and therefore a smaller filter. Together, the smaller charge and smaller filter thereby facilitate a smaller gas inflator system. Furthermore, the gas generant compositions of the present invention have burn rates and ignitability that meet and surpass performance criteria for use within a passenger restraint system, thereby reducing performance variability.

As shown in Example 10, it has also been found that the use of nitroguanidine functions to retard the volumetric phase changes normally exhibited by pure ammonium nitrate, thereby further stabilizing the PSAN.

An unexpected benefit of the present chemical compositions is thermal stability. The thermal stability of the gas generants is unexpected based on the poor stability of other fuels and in particular, triazoles and tetrazoles, when combined with PSAN. In contrast to other thermally stable compositions consisting of NQ and PSAN, these compositions ignite readily and without delay and have a burn rate greater than 0.40-0.50 ips at 1000 psi. Furthermore, the amine salts of tetrazoles and triazoles are neither explosive nor flammable and can be transported as non-hazardous chemicals.

The present invention is illustrated by the following examples. All compositions are given in percent by weight.

EXAMPLE 1 - Comparative Example

A mixture of ammonium nitrate (AN), potassium nitrate (KN), and guanidine nitrate (GN) was prepared having 45.35% NH_4NO_3 , 8.0% KN, and 46.65% GN. The ammonium nitrate was phase stabilized by coprecipitating with KN.

The mixture was dry-blended and ground in a ball mill. Thereafter, the dry-blended mixture was compression-molded into pellets. The burn rate of the composition was determined by measuring the time required to burn a cylindrical

pellet of known length at constant pressure. The burn rate at 1000 pounds per square inch (psi) was .257 inches per second (in/sec); the burn rate at 1500 psi was .342 in/sec. The corresponding pressure exponent was 0.702.

5 **EXAMPLE 2 - Comparative Example**

A mixture of 46.13% NH_4NO_3 , 8.14% KN, 35.73% GN, and 10.0% nitroguanidine (NQ) was prepared and tested as described in Example 1. The burn rate at 1000 psi was 0.282 in/sec and the burn rate at 1500 psi was 0.368 in/sec. The corresponding
10 pressure exponent was 0.657.

EXAMPLE 3 - Comparative Example

A mixture of 46.91% NH_4NO_3 , 8.28% KN, 24.81% GN, and 20.0% NQ was prepared and tested as described in Example 1. The burn rate at 1000 psi was 0.282 in/sec and the burn rate at
15 1500 psi was 0.373 in/sec. The corresponding pressure exponent was 0.680.

EXAMPLE 4 - Comparative Example

A mixture of 52.20% NH_4NO_3 , 9.21% KN, 28.59% GN, and 10.0% 5-aminotetrazole (5AT) was prepared and tested as
20 described in Example 1. The burn rate at 1000 psi was 0.391 in/sec and the burn rate at 1500 psi was 0.515 in/sec. The corresponding pressure exponent was 0.677.

EXAMPLE 5 - Comparative Example

Table 1 illustrates the problem of thermal
25 instability when typical nonazide fuels are combined with PSAN:

Table 1: Thermal Stability of PSAN - Non-Azide Fuel Mixtures

Non-Azide Fuel(s) Combined with PSAN	Thermal Stability
5-aminotetrazole (5AT)	Melts with 108C onset and 116C peak. Decomposed with 6.74% weight loss when aged at 107C for 336 hours. Poole '272 shows melting with loss of NH ₃ when aged at 107C.
5 ethylene diamine dinitrate, nitroguanidine (NQ)	Poole '272 shows melting at less than 100C
5 5AT,NQ	Melts with 103C onset and 110C peak.
10 5AT,NQ guanidine nitrate (GN)	Melts with 93C onset on 99C peak.
GN, NQ	Melts with 100C onset and 112C. Decomposed with 6.49% weight loss when aged at 107C for 336 hours.
GN, 3-nitro-1,2,4-triazole (NTA)	Melts with 108C onset and 110C peak.
NQ, NTA	Melts with 111C onset and 113C peak.
15 aminoguanidine nitrate	Melts with 109C onset and 110C peak.
1H-tetrazole (1HT)	Melts with 109C onset and 110C peak.
dicyandiamide (DCDA)	Melts with 114C onset and 114C peak.
GN, DCDA	Melts with 104C onset and 105C peak.
NQ, DCDA	Melts with 107C onset and 115C peak. Decomposed with 5.66% weight loss when aged at 107C for 336 hours.
20 5AT, GN	Melts with 70C onset and 99C peak.
magnesium salt of 5AT (M5AT)	Melts with 100C onset and 111C peak.

In this example, "decomposed" indicates that pellets of the given formulation were discolored, expanded, fractured, and/or stuck together (indicating melting), making them unsuitable for use in an air bag inflator. In general, any PSAN-nonazide fuel mixture with a melting point of less than

115C will decompose when aged at 107C. As shown, many compositions that comprise well known nonazide fuels and PSAN are not fit for use within an inflator due to poor thermal stability.

5 EXAMPLE 6 - Comparative Example

A mixture of 56.30% NH_4NO_3 , 9.94% KN, 17.76% GN, and 16.0% SAT was prepared and tested as described in Example 1. The burn rate at 1000 psi was 0.473 in/sec and the burn rate at 1500 psi was 0.584 in/sec. The corresponding pressure exponent was 0.518. The burn rate is acceptable, however, compositions containing GN, 5-AT, and PSAN are not thermally stable as shown in Table 1, EXAMPLE 5.

EXAMPLE 7

Table 2: Gas Generating Characteristics of GZT, NQ, and PSAN.

15	PSAN (wt%)	78.22	75.83	73.45	71.06	68.68	66.29
	GZT (wt%)	21.78	19.17	16.55	13.94	11.32	8.71
	NQ (wt%)	0.00	5.00	10.00	15.00	20.00	25.00
20	Gas Conversion (wt%)	96.36	96.47	69.58	96.69	96.80	96.91
	Gas Yield (mol/100g GG)	4.06	4.05	4.04	4.04	4.03	4.02
	Gaseous N_2	37.8	37.7	37.6	37.5	37.5	37.4
	Products CO_2	7.6	7.9	8.1	8.4	8.7	9.0
25	(vol.%) H_2O	54.7	54.5	54.3	54.0	53.8	53.6
	Solid Products K_2O (g/100g GG)	3.64	3.53	3.42	3.31	3.20	3.09
30	Flame Temperature (K)	2254	2275	2296	2317	2337	2358

As shown in table 2, gas generant compositions consisting essentially of GZT, NQ, and PSAN generate mostly gas and minimal solids when combusted.

EXAMPLE 8Table 3a: Gas generants comprising BHT-2NH₃ or GZT, and PSAN.

	PSAN 10% KN (wt%)				74.25
5	PSAN 15% KN (wt%)	76.43	75.40	72.32	75.60
	BHT-2NH ₃ (wt%)	23.57	24.60	27.68	
10	BHT-2GAD (wt%)			24.40	
	GZT (wt%)				25.75
	NQ (wt%)				
	Gas Yield	95	95	95	97
15	Melting Point (C)	158	159	159	131
	Aging at 107C	No Deco.	No Deco.	No Deco.	No Deco.
	Ignitability	Exc.	Exc.	Exc.	Exc.
20	Tailorability of Ballistic Properties	Marg.	Marg.	Marg.	Marg.
	Flame Temperature	2179	2156	2074	2052
25	Rb1000 (ips)	0.48	0.47	0.52	0.57
					0.51

Table 3b: Gas generants comprising BHT-2NH₃, PSAN, and NQ.

	PSAN 10% KN (wt%)	64.40	70.28	67.17	65.23	68.08	64.05	71.83
5	PSAN 15% KN (wt%)							
	BHT-2NH ₃ (wt%)	9.60	16.72	19.83	19.77	20.92	22.95	23.17
10	BHT- 2GAD (wt%)							
	GZT (wt%)							
15	NQ (wt%)	26.00	13.00	13.00	15.00	11.00	13.00	5.00
	Gas Yield (wt %)	97	97	97	97	97	97	97
20	Melting Point (C)	131	132	131	131	131	131	131
	Aging at 107C	No Deco.	No Deco.	No Deco.	No Deco.	No Deco.	No Deco.	No Deco.
25	Ignita- bility	Marg.	Exc.	Exc.	Exc.	Exc.	Exc.	Exc.
	Tailor- ability of Ballistic Propert.	Exc.	Exc.	Exc.	Exc.	Exc.	Exc.	Exc.
30	Flame Temp. (°C)	2346	2274	2186	2167	2174	2093	2170
35	Rb1000 (ips)	0.43	0.49	0.52	0.49	0.54	0.52	0.54

Table Reference:

No Deco. = No Decomposition
 Exc. = Excellent
 Marg. = Marginal

Applicants have found that it is difficult to tailor the ballistic performance of inflators containing gas generants consisting of PSAN and an amine or amide salt(s) of tetrazole or triazole. Applicants have also discovered that in addition to
5 excellent burn rates and ignitability, the addition of nitroguanidine to these compositions facilitates simplified tailorability of ballistic performance, thereby making inflator design much simpler. As shown in Tables 3a and 3b, the ballistic
10 tailorability of compositions comprised of PSAN and amine salts of tetrazoles is substantially improved by the addition of NQ. Example 9 further illustrates this.

When formulating these compositions, it was unexpected that with the addition of nitroguanidine, the mixture would still be thermally stable at 107C, and experience essentially no
15 decrease in ignitability or burn rate.

EXAMPLE 9

Figure 1 graphically illustrates the desirability of maintaining NQ in percentages below 35%, and more preferably below 26%. Five curves illustrate the effect of increasing the
20 percentage of NQ from 0-26 weight percent. Table 4 lists data corresponding to each curve, wherein NQ is combined with BHT-2NH₂. These compositions were pressed into pellets, loaded into an airbag inflator, and fired in a 60L tank. In each of the
25 following tests, all variables (pellet size, inflator configuration, etc.) were held constant, except for the formulation. Table 4 reflects testing that showed no significant change in any of the other desirable properties such as high gas yield, low solids, thermal stability, and burn rate.

Table 4: Ballistic Tailorability

Curve	NQ (wt %)	BHT-2NH ₃ + PSAN (wt %)	Time to 1 kPa (ms)	Maximum Slope (kPa/ms)	Peak Tank P (kPa)
1	0	100	5.7	20.2	203.5
2	11	89	3.4	15.5	193.0
3	13	87	5.3	13.0	187.5
4	15	85	4.2	11.3	176.5
5	26	74	12.2	6.9	68.2

The time to a tank pressure of 1kPa (known as time to first gas in the industry), the maximum slope, and the peak tank pressure are all used to describe the ballistic performance of an airbag inflator. It can be seen that as the amount of NQ in the composition increases, both the maximum slope and the peak tank pressure decrease. The time to first gas is at an acceptable level of 3ms to 6ms in curves 1-4. The time to first gas in curve 5 is at an undesirable high level, and is indicative of a delay in ignition of the gas generant. This demonstrates the poor ignitability of gas generant compositions containing higher percentages of NQ. The ignition delay seen in curve 5 can be corrected by operating at a higher inflator internal combustion pressure. However, this would result in the need for a much more robust inflator structure thereby increasing the size and weight of the inflator.

EXAMPLE 10

Another unexpected result, as shown in Figure 2, is that nitroguanidine appears to help stabilize ammonium nitrate against volumetric phase changes during thermal cycling. A composition containing 49% AN, 9% KN, and 43% NQ was prepared by grinding and blending the dry materials together. The AN in this composition was unstabilized since the AN and KN were not combined to form a solution. This composition was tested by DSC and compared to pure AN. At room temperature, AN phase IV exists. Upon heating phase IV changes into phase II at about 55°C. This is clearly seen on the DSC for pure AN. For the

composition containing AN and NQ, the phase change has been eliminated and does not occur below 110°C. It is believed that lower amounts of NQ will provide the same benefit of AN phase-stabilization.

5 **EXAMPLE 11**

 A composition resulting from the mixture of gas generant constituents consisting of 70.28% PSAN, 16.72% BHT-2NH₃, and 13.00% NQ was prepared and pressed into pellets. The pellets were placed in a covered, but unsealed container in a helium-purged chamber and aged at 107°C. In this way, any volatiles formed during decomposition would result in a weight loss in the sample. After 408 hours of aging, the volatiles weight loss was 0.30%. After 2257 hours of aging, the volatiles weight loss was 0.97%. After aging, the pellets showed no physical signs of decomposition. In addition, thermal analysis (DSC) showed no significant differences in the pellets before and after aging. The pellets which were aged for 2257 hours at 107°C were tested in an inflator and showed no significant differences in ballistic performance when compared to unaged pellets.

20 **EXAMPLE 12**

 A composition resulting from the mixture of gas generant constituents consisting of 67.17% PSAN, 19.83% BHT-2NH₃, and 13.00% NQ was prepared and pressed into pellets. The PSAN was a co-crystallized mixture of 90% AN and 10% KN. The pellets were placed in sealed inflators and temperature cycled. One cycle consisted of holding the inflators at 105°C for two hours, cooling to -40°C in two hours, holding for two hours, and heating to 105°C in two hours. After 50 cycles, the inflators were tested and showed no significant difference from the baseline units in ballistic performance. The physical appearance of the pellets after cycling was unchanged; there were no expansion or cracks as is normally seen in unstabilized AN.

 Although the components of the present invention have been described in their anhydrous form, it will be understood that the teachings herein encompass the hydrated forms as well.

While the foregoing examples illustrate and describe the use of the present invention, they are not intended to limit the invention as disclosed in certain preferred embodiments herein. Therefore, variations and modifications commensurate
5 with the above teachings and the skill and/or knowledge of the relevant art, are within the scope of the present invention.

WE CLAIM:

1. A gas generant composition for a gas generator of a vehicle passenger restraint system comprising a hydrated or anhydrous mixture of:

nitroguanidine and one or more nonazide high-nitrogen
5 fuels selected from a group consisting of
guanidines, tetrazoles, triazoles, salts of
tetrazole, and salts of triazole; and

an oxidizer selected from the group consisting of
10 phase stabilized ammonium nitrate and ammonium
perchlorate.

2. A gas generant composition as claimed in Claim 1 further comprising:

a burn rate modifier selected from a group comprising
alkali, alkaline earth, and transitional metal
5 salts of tetrazoles and triazoles,
triaminoguanidine nitrate, alkali and alkaline
earth metal nitrates and nitrites, dicyandiamide,
alkali and alkaline earth metal salts of
dicyandiamide, alkali and alkaline earth
10 borohydrides, and mixtures thereof.

3. A gas generant composition as claimed in Claim 1 further comprising:

a combination slag former and coolant selected from a
group comprising clay, silica, glass, alumina,
5 and mixtures thereof.

4. A gas generant composition as claimed in Claim 1 further comprising:

a burn rate modifier selected from a group comprising
alkali, alkaline earth, and transitional metal
5 salts of tetrazoles and triazoles,
triaminoguanidine nitrate, alkali and alkaline
earth metal nitrates and nitrites, dicyandiamide,
alkali and alkaline earth metal salts of

10 dicyandiamide, alkali and alkaline earth
borohydrides, and mixtures thereof; and
a combination slag former and coolant selected from a
group comprising clay, silica, glass, alumina,
and mixtures thereof.

5. A gas generant composition as claimed in Claim 1
wherein:

5 said nitroguanidine in combination with said nonazide
high nitrogen fuels comprises 15%-60% by weight
of said mixture; and
said oxidizer comprises 40%-85% by weight of said
mixture.

6. A gas generant composition as claimed in Claim 1
wherein:

5 said nitroguanidine comprises 1%-30% by weight of said
mixture;
said nonazide high-nitrogen fuel comprises 4%-40% by
weight of said mixture; and
said oxidizer comprises 40%-85% by weight of said
mixture.

7. The composition of claim 1 wherein said nonazide fuels
are selected from a group consisting of 5-nitrotetrazole, 5,5'-
bitetrazole, nitroaminotriazole, nitrotriazoles, nitrotetrazoles
and 3-nitro-1,2,4 triazole-5-one.

5 8. The composition of claim 1 wherein said nonazide fuels
are selected from the group consisting of 1-, 3-, and 5-
substituted nonmetal salts of triazoles, and, 1- and 5-
substituted nonmetal salts of tetrazoles; said salts consisting
of nonmetallic cationic and anionic components, and, said salts
substituted with hydrogen or a nitrogen-containing compound.

9. The composition of claim 8 wherein said nitrogen-
containing compound is selected from a class consisting of amino,
nitro, nitramino, tetrazolyl and triazolyl groups, said salts

substituted directly or via amine, diazo, or triazo groups; and,
5 said cationic component is from a member of a class of nitrogen
containing compounds selected from a group consisting of amines,
aminos, and amides.

10. The composition of claim 8 wherein said cationic
component is formed from a member of the group consisting of
ammonia, carbonylhydrazide, oxamic hydrazide, and hydrazine;
guanidine compounds consisting of guanidine, aminoguanidine,
5 diaminoguanidine, triaminoguanidine, dicyandiamide and
nitroguanidine; amides consisting of urea, oxamide, bis-
(carbonamide) amine, azodicarbonamide, and hydrazodicarbonamide;
and amino azoles such as 3-amino-1,2,4-triazole, 3-amino-5-nitro-
1,2,4-triazole, 5-aminotetrazole, 3-nitramino-1,2,4-triazole, 5-
10 nitraminotetrazole, and melamine.

11. The composition of claim 8 wherein said nonmetal salts
of tetrazole are selected from the group consisting of
monoguanidinium salt of 5,5'-Bis-1H-tetrazole, diguanidinium salt
of 5,5'-Bis-1H-tetrazole, monoaminoguanidinium salt of 5,5'-Bis-
5 1H-tetrazole, diaminoguanidinium salt of 5,5'-Bis-1H-tetrazole,
monohydrazinium salt of 5,5'-Bis-1H-tetrazole, dihydrazinium salt
of 5,5'-Bis-1H-tetrazole, monoammonium salt of 5,5'-bis-1H-
tetrazole, diammonium salt of 5,5'-bis-1H-tetrazole, mono-3-
amino-1,2,4-triazolium salt of 5,5'-bis-1H-tetrazole, di-3-amino-
10 1,2,4-triazolium salt of 5,5'-bis-1H-tetrazole, and
diguanidinium-5,5'-azotetrazolate.

12. The composition of claim 8 wherein said nonmetal salts
of triazole are selected from the group consisting of
monoammonium salt of 3-nitro-1,2,4-triazole, monoguanidinium salt
of 3-nitro-1,2,4-triazole, diammonium salt of dinitrobitriazole,
5 diguanidinium salt of dinitrobitriazole, and monoammonium salt
of 3,5-dinitro-1,2,4-triazole.

13. The composition of claim 1 wherein said gas generant
consists essentially of nitroguanidine, diguanidinium-5,5'-
azotetrazolate, and phase stabilized ammonium nitrate.

14. The composition of claim 1 wherein said gas generant consists essentially of nitroguanidine, diammonium salt of 5,5'-bis-1H-tetrazole, and phase stabilized ammonium nitrate.

15. A composition of claim 1 consisting essentially of nitroguanidine, monoguanidinium salt of 5,5'-Bis-1H-tetrazole, and phase stabilized ammonium nitrate.

16. A composition of claim 1 consisting essentially of nitroguanidine, diguanidinium salt of 5,5'-Bis-1H-tetrazole, and phase stabilized ammonium nitrate.

17. A composition of claim 1 consisting essentially of nitroguanidine, monoaminoguanidinium salt of 5,5'-Bis-1H-tetrazole, and phase stabilized ammonium nitrate.

18. A composition of claim 1 consisting essentially of nitroguanidine, diaminoguanidinium salt of 5,5'-Bis-1H-tetrazole, and phase stabilized ammonium nitrate.

19. A composition of claim 1 consisting essentially of nitroguanidine, monohydrazinium salt of 5,5'-Bis-1H-tetrazole, and phase stabilized ammonium nitrate.

20. A composition of claim 1 consisting essentially of nitroguanidine, dihydrazinium salt of 5,5'-Bis-1H-tetrazole, and phase stabilized ammonium nitrate.

21. A composition of claim 1 consisting essentially of nitroguanidine, monoammonium salt of 5,5'-bis-1H-tetrazole, and phase stabilized ammonium nitrate.

22. A composition of claim 1 consisting essentially of nitroguanidine, diammonium salt of 5,5'-bis-1H-tetrazole, and phase stabilized ammonium nitrate.

23. A composition of claim 1 consisting essentially of

nitroguanidine, mono-3-amino-1,2,4-triazolium salt of 5,5'-bis-1H-tetrazole, and phase stabilized ammonium nitrate.

24. A composition of claim 1 consisting essentially of nitroguanidine, di-3-amino-1,2,4-triazolium salt of 5,5'-bis-1H-tetrazole, and phase stabilized ammonium nitrate.

25. A gas generant composition for a gas generator of a vehicle passenger restraint system resulting from a mixture of hydrated or anhydrous gas generant constituents, said constituents comprising:

5 nitroguanidine and one or more nonazide high-nitrogen
 fuels selected from a group consisting of
 guanidines, tetrazoles, triazoles, salts of
 tetrazole, and salts of triazole; and
10 an oxidizer selected from the group consisting of
 phase stabilized ammonium nitrate and ammonium
 perchlorate.

26. The composition of claim 25 wherein:

 said nitroguanidine in combination with said nonazide
 high nitrogen fuels comprises 15%-60% by weight
 of said mixture; and
5 said oxidizer comprises 40%-85% by weight of said
 mixture.

27. The composition of claim 25 wherein:

 said nitroguanidine comprises 1%-30% by weight of said
 mixture;
 said nonazide high-nitrogen fuel comprises 4%-40% by
5 weight of said mixture; and
 said oxidizer comprises 40%-85% by weight of said
 mixture.

28. The composition of claim 25 wherein said nonazide fuels
are selected from a group consisting of 5-nitrotetrazole, 5,5'-
bitetrazole, nitroaminotriazole, nitrotriazoles, nitrotetrazoles
and 3-nitro-1,2,4 triazole-5-one.

29. The composition of claim 25 wherein said nonazide fuels are selected from the group consisting of 1-, 3-, and 5-substituted nonmetal salts of triazoles, and, 1- and 5-substituted nonmetal salts of tetrazoles; said salts consisting of nonmetallic cationic and anionic components, and, said salts substituted with hydrogen or a nitrogen-containing compound.

30. The composition of claim 29 wherein said nitrogen-containing compound is selected from the class consisting of amino, nitro, nitramino, tetrazolyl and triazolyl groups, said salts substituted directly or via amine, diazo, or triazo groups; and, said cationic component is formed from a class of nitrogen containing compounds selected from a group consisting of amines, aminos, and amides.

31. The composition of claim 29 wherein said cationic component is formed from a member of a group consisting of ammonia, carbohydrazide, oxamic hydrazide, and hydrazine; guanidine compounds consisting of guanidine, aminoguanidine, diaminoguanidine, triaminoguanidine, dicyandiamide and nitroguanidine; amides consisting of urea, oxamide, bis-(carbonamide) amine, azodicarbonamide, and hydrazodicarbonamide; and amino azoles such as 3-amino-1,2,4-triazole, 3-amino-5-nitro 1,2,4-triazole, 5-aminotetrazole, 3-nitramino-1,2,4-triazole, 5-nitraminotetrazole, and melamine.

32. The composition of claim 29 wherein said nonmetal salts of tetrazoles are selected from the group consisting of monoguanidinium salt of 5,5'-Bis-1H-tetrazole, diguanidinium salt of 5,5'-Bis-1H-tetrazole, monoaminoguanidinium salt of 5,5'-Bis-1H-tetrazole, diaminoguanidinium salt of 5,5'-Bis-1H-tetrazole, monohydrazinium salt of 5,5'-Bis-1H-tetrazole, dihydrazinium salt of 5,5'-Bis-1H-tetrazole, monoammonium salt of 5,5'-bis-1H-tetrazole, diammonium salt of 5,5'-bis-1H-tetrazole, mono-3-amino-1,2,4-triazolium salt of 5,5'-bis-1H-tetrazole, di-3-amino-1,2,4-triazolium salt of 5,5'-bis-1H-tetrazole, and diguanidinium-5,5'-azotetrazolate.

33. The composition of claim 29 wherein said nonmetal salts of triazole are selected from the group consisting of monoammonium salt of 3-nitro-1,2,4-triazole, monoguanidinium salt of 3-nitro-1,2,4-triazole, diammonium salt of dinitrobitriazole, diguanidinium salt of dinitrobitriazole, and monoammonium salt of 3,5-dinitro-1,2,4-triazole.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US97/12579

A. CLASSIFICATION OF SUBJECT MATTER

IPC(6) : C06B 47/08, 31/32, 29/22

US CL : 149/36, 47, 76

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 149/36, 47, 76

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

APS, search terms: tetrazole#, triazole#, psan, phase-stabilized,

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y,P	US 5,545,272 (POOLE ET AL) 13 August 1996, abstract, column 3, line 40-column 7, line 18.	1-22, 25-33
Y	US 5,531,941 A (POOLE) 02 July 1996, abstract, column 3, lines 45-60, column 4, line 60-column 5, line 6, column 5, lines 40-45.	1-23, 25-33
Y	US 5,035,757 A (POOLE) 30 July 1991, column 4, lines 6-18, column 5, line 52-column 6, line 9.	3, 4, 7, 9, 10
Y	US 5,198,046 A (BUCERIUS ET AL) 30 March 1993, abstract, column 3, lines 6-13 and 36-40.	8-11, 13

☒ Further documents are listed in the continuation of Box C. ☐ See patent family annex.

* Special categories of cited documents:

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P document published prior to the international filing date but later than the priority date claimed

T

later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

X

document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

Y

document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

Z

document member of the same patent family

Date of the actual completion of the international search

22 SEPTEMBER 1997

Date of mailing of the international search report

13 NOV 1997

Name and mailing address of the ISA/US
Commissioner of Patents and Trademarks
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INTERNATIONAL SEARCH REPORT

International application No.
PCT/US97/12579

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US 5,472,647 A (BLAU ET AL) 05 December 1995, column 5, lines 51-65, column 6, lines 4-21, column 7, lines 8-14.	12, 14-22, 28-30, 32, 33

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US97/12579

Box I Observations where certain claims were found unsearchable (Continuation of item 1 of first sheet)

This international report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:
2. ☐ Claims Nos.:
because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:
3. ☐ Claims Nos.:
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box II Observations where unity of invention is lacking (Continuation of item 2 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

Please See Extra Sheet.

1. ☒ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.
2. ☐ As all searchable claims could be searched without effort justifying an additional fee, this Authority did not invite payment of any additional fee.
3. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:
4. ☐ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

Remark on Protest ☐ The additional search fees were accompanied by the applicant's protest.
☒ No protest accompanied the payment of additional search fees.

INTERNATIONAL SEARCH REPORT

International application No.

PCT/US97/12579

BOX II. OBSERVATIONS WHERE UNITY OF INVENTION WAS LACKING

This ISA found multiple inventions as follows:

This application contains claims directed to more than one species of the generic invention. These species are deemed to lack Unity of Invention because they are not so linked as to form a single inventive concept under PCT Rule 13.1. In order for more than one species to be searched, the appropriate additional search fees must be paid. The species are as follows:

Group I: Compounds comprising guanidines

Group II: Compounds comprising tetrazoles or salts thereof

Group III: Compounds comprising triazoles or salts thereof

The claims are deemed to correspond to the species listed above in the following manner:

Group I: None

Group II: 7-12,28-33(in part), 13-24

Group III: 7-12,28-33 (in part)

The following claims are generic: 1-6, 25-27.

The species listed above do not relate to a single inventive concept under PCT Rule 13.1 because, under PCT Rule 13.2, the species lack the same or corresponding special technical features for the following reasons: Claim 1 lacks an inventive step under PCT Rule 13.2 and PCT Administrative Instructions, Annex B, Part 1(f)(i)(B)(2) a not being drawn to art recognized equivalents.